

# Re-interpretation of Raman spectra of carbonaceous materials: A molecular approach

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Raman spectroscopy has been widely used to study the structure of different carbonaceous materials, from graphene (Eckman et al. 2012) to soot particles (Sadezky et al. 2005). Carbonaceous material Raman spectra present a first order band in the 1000-1700  $\text{cm}^{-1}$  region. For pure graphite mono-crystals only one band is present, known as G band, around 1580  $\text{cm}^{-1}$ . As the number of defects increases, two new bands appear, generally known as D1 and D2. D1 band, at around 1350  $\text{cm}^{-1}$ , corresponds to a lattice vibration mode which is forbidden by symmetry for perfect graphite. The presence of defects, e.g. the creation of edges due to vacancy defects in the graphene layers, results in a symmetry break and a relaxation of the selection rule. D2 band, at  $\sim 1620 \text{ cm}^{-1}$ , is traditionally assigned to lattice vibrations analogous to that of the G band but involving isolated graphene layers. When the carbonaceous material is highly disordered, two extra bands appear, these bands are known as D3 and D4. D3 band, at  $\sim 1500 \text{ cm}^{-1}$ , is generally very broad and is related to amorphous carbon. D4 band is characteristic for highly disorder materials like soot or coal chars (Sadezky et al. 2005). The assignment of D4 band is still under discussion, some authors attribute it to  $\text{sp}^3\text{-sp}^2$  mixed sites at the periphery of the crystallites or to C-C and C=C stretching vibrations of polyene-like structures (Livneh et al. 2000, Dippel et al. 1999).

Among the different deconvolution models used for interpretation of carbonaceous materials Raman spectra, the most widely used is the one proposed by Sadezky et al. (2005). The authors used a combination of four Lorentzian functions (D1, D2, D4, and G bands) and one Gaussian function (D3 band) (Fig. 1).

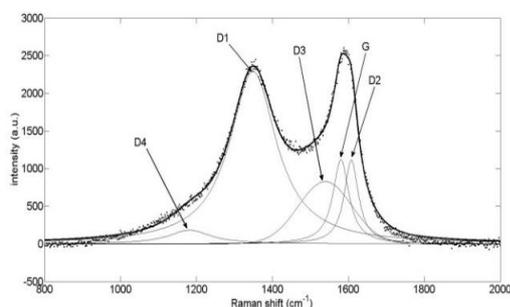


Figure 1. Example of deconvolution of soot Raman spectra using the approach proposed by Sadezky et al.

To get a better insight in the link between the observed Raman spectra of carbonaceous compounds and their molecular structure, we have used quantum chemical methods to calculate Raman spectra of

different polycyclic aromatic hydrocarbons (PAH) as surrogates of the grapheme layers present in these materials. Our calculations found a characteristic vibrational mode for all studied PAHs that corresponds to the C-C stretching of edge carbon atoms (Fig. 2).

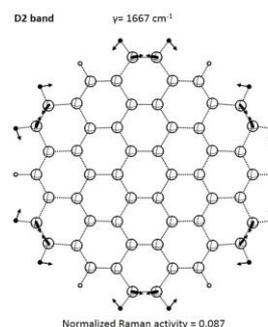


Figure 2. Example of the vibrational mode corresponding to D2 band for circum-coronene( $\text{C}_{54}\text{H}_{18}$ )

This mode is found in all cases at the position where D2 band is observed. Although this band has been traditionally associated with graphene layers surface, while D1 is related to edges, our calculations show how D2 band might be related with edges and not with the surface of graphene domains. The appearance of this mode linked to edge carbons is consistent with the experimental observation reported by Eckman et al. (2012). In this work they link the intensity of D2 band with the formation of small crystalline domains due to vacancy defects in a graphene layer.

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